



REGULAR ARTICLE

Formation of Nitrogen Supersaturated (Nitrogen-Rich) MeN Nitrides at Thermobaric Sintering of PcBN Composites of cBN-{TiN, ZrN, HfN, VN, NbN}-Al Systems

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The crystal structure of MeN nitrides, existing in the surface layers of PcBN composites of cBN-{TiN, ZrN, HfN, VN, NbN}-Al systems (composition, vol. %: cBN: MeN: Al as (60:35:5, vol. %) sintered at high pressure and high temperature (HPHT, 7.7 GPa, 1600-2450 °C), was studied in detail using the X-ray diffraction structural analysis method. It was shown that the crystal structure of each MeN nitride belongs to the modified NaCl type structure with an additional position partially filled by the nitrogen atoms. The presence of such a position leads to a certain excess of nitrogen on the sample's surface, the source of which is nitrides from the depth of the composite. It is shown that the diffusion of nitrogen atoms through defects and lattice sites of MeN crystal lattices from the bulk to the surface of composite plays an important role in the formation of crystal structures of MeN nitrides at the barothermal conditions. Using the results of X-ray diffraction structural calculations as reference values, the main parameters of this diffusion process (activation energy and rate constant) were determined for cBN-{TiN, HfN, VN, NbN}-Al composites. It is shown that the activation energy of diffusion increases in HfN → TiN → VN → NbN series and correlates with the formation enthalpy of each MeN nitrides.

Keywords: High pressure, High temperatures, cBN composite, MeN nitrides, X-ray diffraction, Crystal structure, Nitrogen migration.

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1. INTRODUCTION

Ceramic matrix nanocomposites reinforced with dispersed carbide, boride, nitride or oxide nanoparticles play a pivotal role in a designing of cutting tools. of individual occupy an important place in the creation of cutting tools. It is known that the tools, obtained from PcBN superhard materials of the BH type (more than 80 vol.% cBN) and BL type (30-70 vol.% cBN) are the most widely used cutting tools for high-speed processing of various metal alloys [1-3].

In addition to high thermal and chemical stability provided by cBN grains, the physical and mechanical properties of such cutting tool can be substantially advanced by addition of a certain binding phase to the cBN matrix [4]. Mononitrides of transition metals such as TiN, ZrN, HfN, VN and NbN (NaCl-type structure) are widely used as such binder.

Properties of composite materials of cBN-{TiN, ZrN, VN, NbN}-Al systems were studied in Refs. [5-10]. As a result of XRD studies it was shown that under high pressure (up to 7.7 GPa) and temperatures higher than 2000 °C the solid state interaction of cBN and TiN or ZrN leads to the formation of TiB₂ or ZrB₂ diborides, which improve the mechanical properties of cBN-{TiN, ZrN}-Al composites [5-9].

Diborides VB₂ and NbB₂ are not formed at HPHT sintering of cBN-{VN, NbN}-Al mixtures, but a small amount of MeB monoborides is detected at high temperatures.

SEM examination of the surface of cBN-{TiN, VN}-Al composites sintered at 1850-2300 °C has revealed in the intergranular space the narrow zones of reaction products, which are clearly visible at high magnification. However, SEM images obtained at lower magnification demonstrate a homogeneous microstructure of the samples sintered at 1850-2150 °C as well as display the collective recrystallization of grains at 2300 °C [9].

It is shown that the density of the samples increases significantly from ≈ 3.2-3.5 g/cm³ in the initial mixtures to ≈ 4.1-4.3 g/cm³ in the HPHT sintering products. Moreover, the impact of the sintering temperature increase on samples' density (i.e. porosity of samples) is almost negligible [9].

As sintering temperature increases, the mechanical properties of these composites change to one degree or another. Thus, at temperatures from 1600 to 2350 °C the microhardness of composites with TiN increases from 29 to 32 GPa, reaching its maximum in a range from 2000 to 2150 °C [9], while the microhardness of composites with VN in this temperature range increases monotonically from 22 to 30 GPa.

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The Young's modulus in these composites gradually increases from 580 to 610 GPa for the system with TiN and from 450 to 550 GPa for the system with VN [9]. Besides, other mechanical properties of these composites are also temperature dependent. I.e., the relative change of the shear modulus reaches 30% in cBN-{TiN, VN}-Al composites, and the fracture toughness value is about 10% [9].

The above-described temperature dependences of the mechanical properties of products of HPHT sintering cannot be explained just by the combination of such characteristics as phase composition, microstructure, and density. It would be natural to include other factors in the consideration, one of which is undoubtedly the crystal structure of the nitrides, which are forming the binder of composites.

Previously we have studied in detail the features of the crystal structure of TiN and VN nitrides, existing in BL cBN-{TiN, VN}-Al composites in Refs. [11,12]. In this paper, similar XRD structural calculations were performed to refine the crystal structures of ZrN, HfN and NbN nitrides. The results obtained here for ZrN, HfN and NbN in combination with previous data for TiN and VN [11,12] made it possible to generalize and analyze the effect of barothermal load on nitrides of transition metals of groups IV and V, which form the binder for cBN-MeN-Al composites. (Note: in the composites of the cBN-TaN-Al system there are tantalum nitrides with a crystal structure different from the NaCl type).

2. MATERIALS AND METHODS

Composite samples were obtained by HPHT sintering of mechanically activated charge of cBN: MeN: Al (60: 35: 5, vol. %, MeN = TiN, ZrN, HfN, VN or NbN) in a toroid type apparatus (pressure was 7.7 GPa, temperature range was 1600-2450 °C) at V. Bakul Institute for superhard materials (Kyiv, Ukraine). Diffraction patterns of the composites synthesized were collected with STOE STADI MP diffractometer (CuK α radiation) in a discrete mode with the following scanning parameters: observation range $2\theta = (10-100)^\circ$, step scan is 0.015° and counting time per step is 3 s. The original software package, including full complex of standard Rietveld procedures, has been used for analysis and interpretation of the X-ray diffraction patterns obtained, namely, determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis for phase identification and the least square method for refinement of lattice parameters for each phase; testing of the structure models proposed and refining crystal structure parameters (including coordinates of atoms, atomic position filling, texture, etc.); calculation of the parameters of the real structure of the individual phases (coherent block sizes and microdeformation values).

3. RESULTS AND DISCUSSION

According to the data of XRD phase analysis, at sintering temperatures higher than 1700 °C, the barothermal treatment of the initial cBN-MeN-Al

mixtures leads to the formation of TiB₂, ZrB₂, HfB₂ or NbB borides. A small amount of AlN nitride, as well as ZrO₂ and α -Al₂O₃ oxides were detected in some synthesis products. The refined values of crystal lattice parameters *a* of MeN mononitrides are significantly different not only from the values inherent to these phases in the charge, but also vary with sintering temperature increase (Table 1).

As an illustration, Table 1 presents a plot of the temperature dependence of the TiN lattice parameter (Fig. 1). It should also be noted that the nitrides with different values of lattice parameters (HfN and HfN', as well as NbN and NbN') coexist in cBN-{HfN, NbN}-Al composites at sintering temperatures of ≈ 2150 °C.

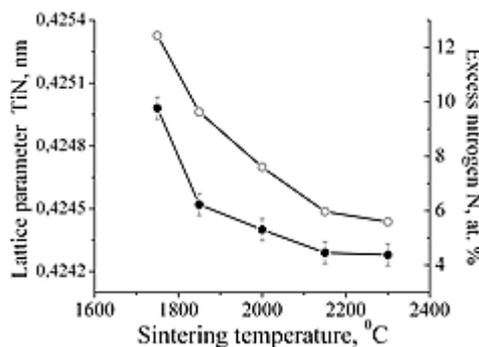


Fig. 1 – A plot of the temperature dependence of the lattice parameter of TiN nitride

To follow the impact of sintering conditions on the experimental temperature dependences of lattice parameters $a(t)$ the lattice distortions ϵ were estimated. The lattice distortion were calculated as $\epsilon(\%) = 100 \cdot (a_t - a_{20})/a_t$, where a_t is the lattice parameter at a certain sintering temperature t , and a_{20} is the lattice parameter of the initial mixture. The obtained ϵ values are listed in Table 1.

Comparison of lattice distortions calculated in this way with microdeformation meanings defined by the approximation method from broadening of corresponding X-ray diffraction reflections for TiN and VN has revealed the proximity of their values (Table 1).

Table 1 – Characteristics of the crystal structure of MeN nitrides, existing in the HPHT cBN-MeN-Al composites sintered at 7.7 GPa

Sintering temperature, t , °C	Lattice parameter, a , nm	Lattice distortion, ϵ , %	Excess nitrogen, δ , at. %
	TiN		
20 ¹⁾	0.4240	0/0.09 ²⁾	0
1750	0.42498	0.231/0.19	12.4
1900	0.42452	0.122/0.09	9.6
2000	0.42440	0.094/0.07	7.6
2150	0.42429	0.068/0.06	6.0
2300	0.42428	0.065/0.06	5.6
2450	–	–	–
	ZrN		
20	0.45730	0	0
1750	0.45762	0.070	1.7
1900	0.45773	0.094	5.2
2000	0.45766	0.079	5.9

2150	0.45761	0.068	7.7
2300	0.45755	0.055	8.5
$t_s, ^\circ\text{C}$	HfN		
20	0.4526	0	0
1900	0.4543	0.374	18.1
2000	0.4542	0.352	16.0
2150	0.4543	0.330	10.1
2300	0.4546 ³⁾	0.511	12.2
2450	0.4550	0.527	21.9
$t_s, ^\circ\text{C}$	VN		
20 ¹⁾	0.4123	0/0.30 ²⁾	0
1750	0.41334	0.252/0.22	10.1
1900	0.41330	0.242/0.16	7.7
2000	0.41319	0.215/0.11	6.3
2150	0.41311	0.196/0.13	4.1
2300	0.41301	0.172/0.17	3.9
2450	0.41296	0.160/0.15	2.3
$t_s, ^\circ\text{C}$	NbN		
20	0.4408	0	0
1750	0.44082	0.0040	1.1
1900	0.44081	0.002	0.4
2000	0.44089	0.020	0
2150	0.44132 ³⁾	0.118	3.5
2300	0.44146	0.149	2.8

¹⁾ Values of lattice parameters of MeN the initial cBN-MeN-Al mixture.

²⁾ For TiN and VN the lattice microdeformations are listed in addition to their lattice distortion values.

³⁾ Data for high-temperature HfN' and NbN' nitrides are listed.

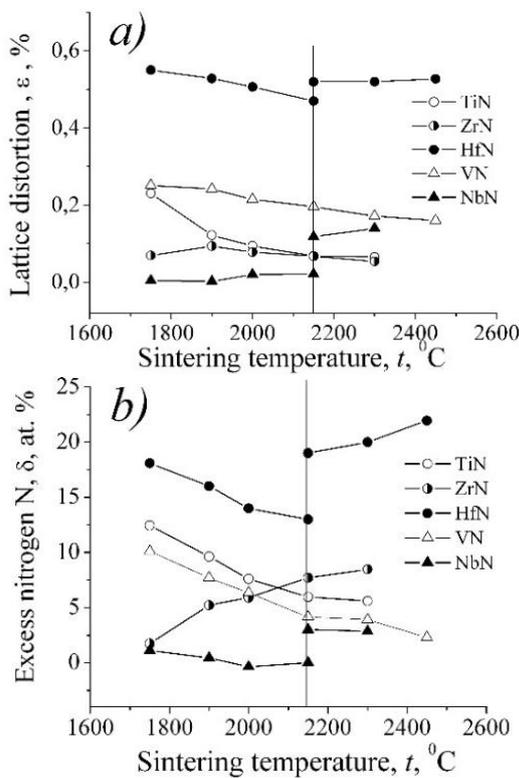


Fig. 2 – Temperature dependences of the distortions ε experienced by the crystal lattices of MeN nitrides during HPHT sintering of cBN-MeN-Al composites (a) and dependences of the nitrogen excess δ in their structure (b)

In general, temperature dependences of distortions $\varepsilon(t)$ that crystal lattices of MeN undergo at HPHT sintering of cBN-MeN-Al composites are illustrated in Fig. 2a. It is clearly seen that $\varepsilon(t)$ either decrease monotonically (TiN, VN) or weakly depend on t (ZrN) in the full range of sintering temperatures. However, $\varepsilon(t)$, which gradually decreased with temperatures up to $\approx 2150\text{ }^\circ\text{C}$ for HfN and NbN, increases abruptly to ε inherent to HfN' or NbN' nitrides.

There is no doubt that the existing increase in lattice parameters of initial nitrides after their HPHT sintering (Table 1), as well as the dependence of the lattice parameters on sintering temperature (Fig. 2a), could indicate certain structural transformations. Thus, structural calculations have shown that the crystal structures of initial MeN nitrides belong to the NaCl type structure and have a small deficit of nitrogen atoms, i.e. the calculated composition of nitrides is $\approx \text{MeN}_{0.95}$.

However, the crystal structures of MeN, existing in HPHT sintering products, belong to a modified NaCl-type structure. The detailed study of this structure was provided in our previous research [11, 12]. Table 2 contains the calculation data on the placement location of Me and N atoms within the framework of the NaCl type structure (initial nitrides) and modified NaCl type structure (nitrides in composites). Correctness of these calculations is evidenced by the value of the reliability factor ($R_B \leq 0.02$).

Analysis and generalization of the data obtained as a result of crystal structure calculations of MeN nitrides from HPHT sintered cBN-MeN-Al products have revealed the following: 1) Metal atoms (Me) completely occupy their position ($q_1 = 1$); 2) Nitrogen atoms (N) are located in two positions that have vacancies ($q_2 < 1, q_3 \ll 1$); 3) Coordinate parameter x depends on the type of metal that forms MeN nitride; 4) Both Al and B atoms do not participate in the formation of MeN crystal structure.

Taking this into account, the composition of each MeN nitride was determined by joint refinement of the filling factors of positions q_2 and q_3 . The nitrogen excess for MeN nitride was calculated in relation to its content in the charge (49 at. % N) (Table 1). Behavior of the calculated value of excess nitrogen δ with sintering temperature of the composites presented in Fig. 2b and Fig. 4 clearly shows that it is the excess of nitrogen that leads to the distortion of the nitride crystal lattice.

Table 2 – Crystal structure data for initial MeN nitrides and nitrides MeN existing in HPHT sintered cBN-MeN-Al composites

Arrangement of atoms in the crystal structures of MeN according to their positions of Fm3m space group (No. 225)
Initial MeN: q_1 -4 Me in 4(a) 0 0 0 q_2 -4 N(1) in 4(b) 0.5 0.5 0.5
MeN in composite: q_1 -4 Me in 4(a) 0 0 0 q_2 -4 N(1) in 4(b) 0.5 0.5 0.5 q_3 -24 N(2) in 24(e) x 0 0

Note:

1. q_1 , q_2 and q_3 are the coefficients of occupation of positions by metal and nitrogen atoms ($q \leq 1$).
2. The x coordinate takes the value ≈ 0.32 or ≈ 0.28 depending on the MeN nitride.

It should also be noted the special behavior of ZrN nitride (Figs. 2b, 4), for which an increase in the sintering temperature is accompanied by an increase in the amount of excess nitrogen while maintaining a small distortion of the lattice (Table 1). Thus, the excess nitrogen calculated by XRD structural analysis actually corresponds to the total amount of nitrogen and oxygen that penetrated ZrN lattice at high sintering temperatures.

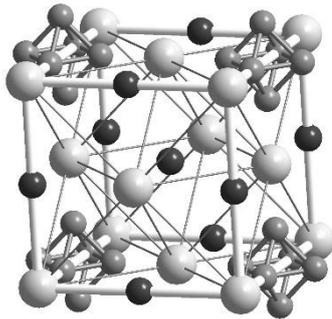


Fig. 3 – Arrangement of atoms in the crystal structures of MeN existing in HPHT sintered cBN-MeN-Al composites (metal atoms Me – big light gray circles, nitrogen atoms N(1) – black circles)

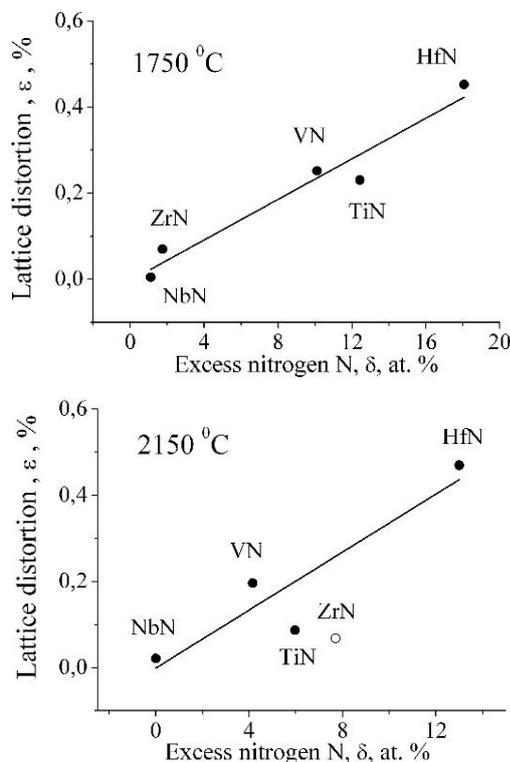


Fig. 4 – Correspondence of the crystal lattice distortion of MeN nitrides, existing in HPHT sintered cBN-MeN-Al composites to an excess of nitrogen

It is important to note the surface character of the phenomenon observed since the conditions of XRD

experiment provide the diffraction pattern from surface layer, i.e. the penetration depth of X-ray radiation is less than 0.1 mm. Previously, the authors of the works [8, 15-17] reported the formation of such nitrogen-enriched layer on the surface of compact samples or films of individual nitrides of transition metals. Obviously, the nitrogen enrichment of MeN nitrides located on the surface of HPHT sintered composites occurs due to its transfer from the internal regions of the sample, i.e., due to diffusion processes.

D. G. Sangiovanni et al. [14] simulated the processes of diffusion of point interstitial defects (migrating nitrogen atoms and lattice vacancies) in TiN nitride using classical molecular dynamics methods (AIMD and CMD). As a result of this simulation, an atomistic process that controls the spontaneous formation of pairs from interstitial N^I nitrogen atoms and N^V crystal lattice vacancies (so-called Frenkel pairs), which can form even in defect-free TiN was described.

This means that N atom of certain lattice leaves its usual position and connects with N atom of the neighboring lattice. According to Ref. [14], about 50 % of these processes also lead to the exchange by of two nitrogen atoms. Occasionally, at the same time, the migrating interstitial nitrogen atom itself can contribute to the formation of a Frenkel pair, tearing out the existing lattice anion with the formation of a new vacancy.

Comparison of the results of the study of MeN crystal structure (Table 2) and theoretical models [14, 15], which describe the diffusional movement of nitrogen atoms, shows that the statistical arrangement of nitrogen atoms in the vertices of octahedra (N^I atoms in position 24e) around the existing vacancy in position 4b (N^V) (Fig. 3) corresponds to the formation of N^I - N^V Frenkel pairs. Moreover, if two Frenkel pairs are formed around such a vacancy, then the neighboring internodal N^I - N^I atoms form a bond, imitating a diatomic N_2 molecule.

That is, barothermal load conditions initiate the diffusion flows of nitrogen atoms (the decay products of MeN and cBN), which moves towards the composite surface due to the temperature gradient in the reaction zone and provides the surface saturation with nitrogen (Table 1, Fig. 2b).

Analysis of the values obtained as a result of the XRD structural study shows that the excess of nitrogen accumulated in MeN on the surface of the composites, at HPHT sintering of the charge (Table 1), correlates with the formation enthalpy of these nitrides (Fig. 5). Namely, the amount of excess nitrogen decreases linearly in the series $HfN \rightarrow TiN \rightarrow VN \rightarrow NbN$ (prone to oxidation ZrN is not considered).

I.e., it is HfN that captures most of the nitrogen that goes to the sample surface with further sublimation as N_2 gas. Moreover, the N_2 molecule is previously formed in the crystal structure of the nitride itself from $N(2)$ atoms located at the adjacent vertices of the octahedron at interatomic distances of ~ 0.11 nm (Fig. 3). It should also be noted that at sintering temperatures higher than 2150 °C, the process of nitrogen accumulation in MeN nitrides is inhibited precisely due to intensification of the formation of free N_2 molecules (Fig. 5).

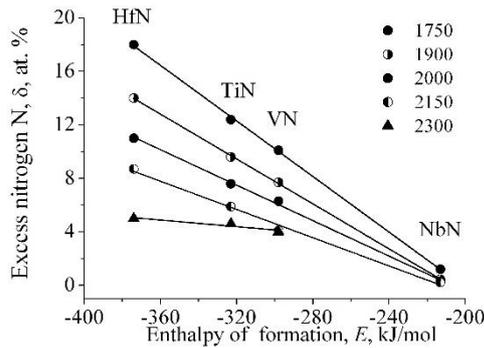


Fig. 5 – Dependence of excess nitrogen accumulated by MeN nitrides on the enthalpy of their formation at certain HPHT sintering temperature

In our opinion, the calculated by XRD method values of excess nitrogen in MeN nitrides, existing on the surface of sintered composites (Table 1), can serve as reference values for the determination of the parameters of nitrogen atom migration from the bulk to the sample's surface.

It is known that diffusion, like the majority of simple processes in a solids (oxidation, chemical reactions, etc.) is well described by the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (1.1)$$

where D is the diffusion coefficient, D_0 is a temperature-independent factor; R is the universal gas constant ($R = 8,3145 \text{ J/mol K}^{-1}$), E_a is the activation energy of diffusion (J/mol), T is the HPHT sintering temperature (K).

Assuming the amount of nitrogen to sample's surface during 1 s of HPHT processing is proportional to $C_N / 45$ (where C_N is the excess of nitrogen in moles, 45 s is the sintering time). Then, this value can be considered as certain analogue of D ($C_N/45 \approx D$) with the accuracy to the factor that describes the area of the diffusion flow. Following the Eq. (1.1), the activation energy of migration of nitrogen atoms from the bulk to the composite's surface can be determined from the graphs plotted in the coordinates $-\ln D$ vs. $1/RT$. Those graphs are linear in the temperature range of 1750 – 2150 °C for TiN, HfN, VN and NbN nitrides, and let us to define the activation energy of nitrogen migration (Table 3, Fig. 5).

The values obtained as a result of the calculations are quite reasonable, since the activation energy of nitrogen diffusion is usually 0.15 and 0.75 eV for the dislocation and bulk mechanisms, respectively.

Table 3 – Characteristics of the nitrogen migration in HPHT sintered cBN- $\{\text{TiN, HfN, VN, NbN}\}$ -Al composites

Nitride	Enthalpy of formation, E , kJ/mol	Diffusion activation energy, Q , kJ/mol	Diffusion activation energy ¹⁾ , Q , eV	Diffusion factor ²⁾ , D_0 , mol/s
HfN	-374	33.5	0.347	5.25×10^{-2}
TiN	-323	72.9	0.756	3.36×10^{-3}
VN	-298	85.7	0.888	1.27×10^{-3}
NbN	-213	168.9	1.750	8.00×10^{-7}

- 1) Diffusion activation energy per individual nitrogen particle.
- 2) The diffusion factor corresponds to the rate of nitrogen atoms migration.

It should be noted that only nitrogen, which was captured by nitrides on the composite's surface, was taken into account when calculating the diffusion parameters (Table 3). The same slope of $\delta(E)$ dependences for temperatures of 1750-2150 °C (Fig. 6) allows us to assume that the release of nitrogen in the form of free N_2 gas is insignificant at these HPHT sintering temperatures. Intensive release of nitrogen outside the sample begins only at temperatures higher than 2150 °C (slope of $\delta(E)$ dependence changes significantly at 2300 °C).

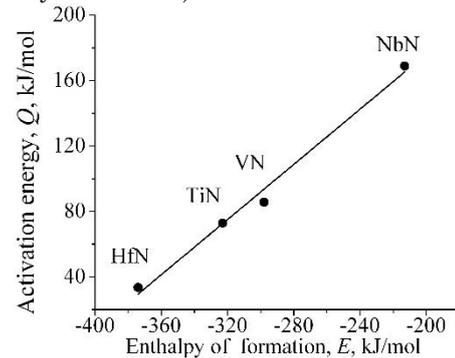
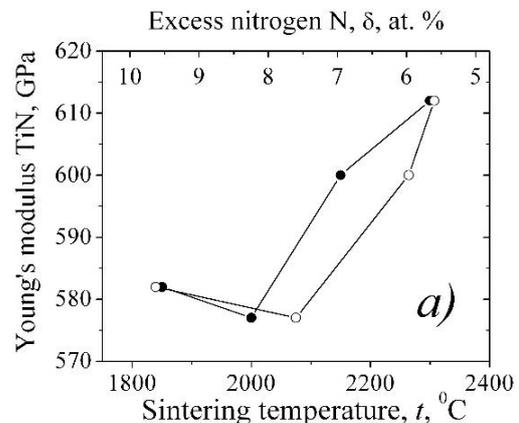


Fig. 6 – Dependence of the activation energy of nitrogen diffusion in MeN nitrides during HPHT sintering of cBN- $\{\text{TiN, HfN, VN, NbN}\}$ -Al composites on the enthalpy of their formation

It is likely, that MeN nitrides compatible with cBN act as a source of additional nitriding of the sample's surface under HPHT sintering. Such nitrogen enrichment of the surface of cBN-MeN-Al composites should have a positive effect on some of its surface properties, such as nanohardness, wear resistance, and corrosion resistance. Thus, H. Xie et al. [8], studying the cBN-TiN composite, showed that the average microhardness on its surface is somewhat higher than in the bulk, namely, for the studied sample, these values are 33.23 and 32.24 GPa, on the surface and in the bulk, respectively.



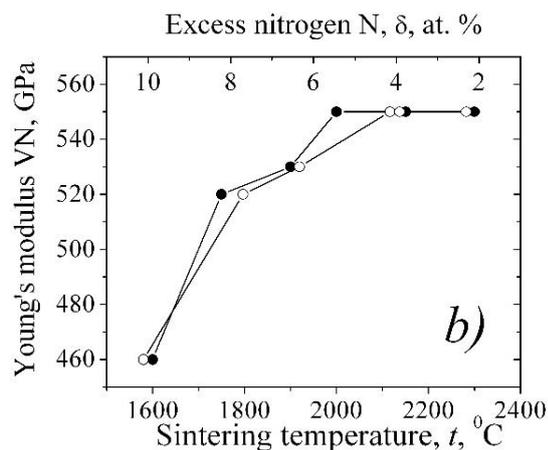


Fig. 7 – Dependence of the activation energy of nitrogen diffusion in MeN nitrides during HPHT sintering of cBN-(TiN, HfN, VN, NbN)-Al composites on the enthalpy of their formation

XRD and electron microscopy studies have shown [9] that the phase composition of HPHT sintered cBN-(TiN, VN)-Al composites as well as their microstructure (on the surface) and density are almost unchangeable in the temperature range of 1750-2300 °C. However, the main macrocharacteristics of composites such as the Vickers hardness, the Young's modulus, shear modulus, fracture toughness are slightly different. Taking into account that $\alpha(T)$ and $\delta(T)$ demonstrate the same behavior for TiN and VN (Fig. 2), the dependence of microcharacteristics mentioned above on the nitrogen excess defined by XRD was considered for cBN-(TiN, VN)-Al composites (Table 1).

For comparison, the Young's modulus meanings are plotted in dependence on an increase of sintering temperature and on a decrease of nitrogen excess for TiN and VN (Fig.7). However, the graphs on Fig. 7 are just illustrative since the nitrogen excess in nitrides changes monotonically with the sintering temperature (Fig. 2b).

At the same time, the enrichment by nitrogen of MeN surface nitrides results in the depletion of bulk (central) regions. That probably, can affect such volumetric macrocharacteristics of the material as the Vickers hardness, the Young's modulus, shear modulus and fracture resistance. S. Yu et al. [18] have calculated these mechanical characteristics in dependence on the nitrogen content in TiN from the first principles.

As a result, it was predicted that the change in nitrogen content in TiN from 50 to 40 at. % leads degradation of mechanical characteristics (at normal pressure): the Young's modulus decreases from 533 to 347 GPa, hardness changes from 24 to 16 GPa, and shear modulus goes down from 215 to 138 GPa (the relative change of these values is about 30%) [18]. For HPHT sintered cBN-(TiN, VN)-Al composites, the experimental meanings of these parameters [9] also gradually decrease with depletion of the sample's

volume with nitrogen, but their relative change does not exceed 15%.

The authors of Ref. [18] theoretically predict that at high pressures (60 GPa) the nitride of TiN₂ can be stable due to existence in the structure of so-called encapsulated N dumbbells with an interatomic distance of ≈ 0.13 nm. The same N₂ dumbbells exist in the model of the modified NaCl type structure proposed by us for the nitrogen-saturated MeN nitrides (Table 2).

A detailed XRD study of the crystal structure of the MeN nitrides, which existing in HPHT syntered cBN-MeN-Al composites (MeN = TiN, ZrN, HfN, VN, NbN; cBN:MeN:Al as 60:35:5 (vol. %)), has revealed the following:

1. The crystal structure of MeN_{0.95} nitrides presented in the cBN-MeN-Al initial charges pretreated in a planetary ball mill belongs to the NaCl type structure.
2. The crystal structure of the nitrides existing in HPHT sintered (7.7 GPa, temperature range of 1600-2450 °C) composites is described in the structural model of the modified NaCl type structure, which contains an additional position for the placement of nitrogen atoms. The partial filling of this position leads to the accumulation of a certain excess of the nitrogen in MeN nitrides.
3. Aluminum from of the charge is not included in the crystalline structures of MeN nitrides, but it reacts with free nitrogen or residual oxygen to form AlN nitride and Al₂O₃ oxide.
4. It is shown that under the conditions of barothermal influence, a significant role in the formation of crystal structures of MeN nitrides located on the composite surface, is played by the diffusion of nitrogen atoms through defects and internodes of their crystal lattices from the internal volume of the composites to their surface. Using the data of XRD structural calculations as reference values, the main parameters of this diffusion process (diffusion activation energy and rate constant) were determined for the cBN-(TiN, HfN, VN, NbN)-Al composites. It is shown that the activation energy of the diffusion increases in the series HfN→TiN→VN→NbN and it correlates with the enthalpy of formation of each of the MeN nitrides.

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Формування пересичених азотом нітридів в умовах термобаричного спікання BL композитів систем cBN-{TiN, ZrN, HfN, VN, NbN}-Al

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З використанням методу рентгеноструктурного аналізу докладно досліджено кристалічну структуру нітридів MeN, які існують в поверхневих шарах HPHT (high pressure, high temperature) спечених (7,7 ГПа, 1600-2450 °C) PcBN композитів систем cBN-{TiN, ZrN, HfN, VN, NbN}-Al складу (об. % cBN:MeN:Al як 60:35:5). Встановлено, що кристалічна структура кожного нітриду MeN описується в структурній моделі модифікованої структури типу NaCl, яка має для атомів азоту додаткову позицію, часткове заповнення якої веде до накопичення на поверхні зразків певного надлишку азоту, джерелом якого виступають нітриди з глибини композиту. Показано, що в умовах баротермічного впливу суттєву роль в формуванні кристалічних структур нітридів MeN відіграє процес дифузії атомів азоту по дефектам та міжвузлям їх кристалічних ґраток з внутрішнього об'єму композитів на їх поверхню. Використовуючи в якості опорних величин дані рентгеноструктурних розрахунків, для композитів систем cBN-{TiN, HfN, VN, NbN}-Al визначено основні параметри цього дифузійного процесу (енергію активації дифузії та константу швидкості). Показано, що енергія активації дифузійного процесу збільшується в ряду HfN → TiN → VN → NbN та корелює з ентальпією утворення кожного з нітридів.

Ключові слова: Високі тиски, PcBN композит, Нітрид MeN, Рентгенівська дифрактометрія, Кристалічна структура, Міграція азоту.